# DEVELOPMENT OF A DIRECT REACTIVITY MEASUREMENT METHOD FOR VOLATILE ORGANIC COMPOUNDS

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## Outline

- Background: Factors affecting $O_3$ Reactivity of VOCs; Mechanism Evaluation Needs

- Direct Reactivity: What it is; How to Measure; Relationship to Other Reactivity Measures

- Experimental Approaches Examined

- Results

- Ongoing Work

- Conclusions

# VOC REACTIVITY

The atmospheric oxidation reactions of Volatile Organic Compounds (VOCs) result in enhanced formation of ground-level ozone from $NO_x$.

VOCs differ in their effects on ozone formation. The term **reactivity** is used to refer to this.

Several aspects of a VOC's atmospheric reactions affect its $O_3$ reactivity:

- Direct Effects:
  - How fast it reacts;
  - How much $O_3$ is formed directly from its reactions and those of its products
- Indirect Effects
  - Whether it enhances or inhibits radicals. Affects how fast $O_3$ is formed from all VOCs
  - Whether it enhances rates of $NO_x$ removal. This affects ultimate $O_3$ yields when $NO_x$ is limited.

**The VOCs effect on $O_3$ also depends on the nature of the environment where it reacts**

# QUANTIFICATION OF REACTIVITY

A useful measure of the effect of a VOC on ozone formation is **incremental reactivity**:

$$\text{Incremental Reactivity of a VOC in an Episode} = \lim_{[VOC] \to 0} \frac{\begin{array}{c}\text{O}_3 \text{ Formed} \\ \text{when VOC} \\ \text{added to} \\ \text{Episode}\end{array} - \begin{array}{c}\text{O}_3 \\ \text{Formed} \\ \text{in an} \\ \text{Episode}\end{array}}{\begin{array}{c}\text{Amount of VOC Added} \\ \text{to Emissions in Episode}\end{array}}$$

**This depends on the conditions of the episode as well as on the VOC**

Because of this, atmospheric reactivities must be calculated using computer airshed models, given:

- Models for airshed conditions

- Chemical Mechanisms for the VOC's atmospheric reactions

**Such calculations can be no more reliable than the chemical mechanism used**

Experiments are needed to test the reliability of mechanisms to predict atmospheric reactivity

# ENVIRONMENTAL CHAMBER EXPERIMENTS

Environmental chamber reactivity experiments have been the primary means used to evaluate mechanisms for predicting effects of VOCs on $O_3$

These involve determining effect of adding the VOC to standard "ROG Surrogate - $NO_x$ - air irradiation experiments.

Using different kinds of ROG surrogates and ROG/$NO_x$ ratios give results that have different sensitivities to different mechanism aspects.

- High ROG/$NO_x$ "Mini-Surrogate" experiments most sensitive to radical effects

- Standard "Full Surrogate" experiments give best correlation to atmospheric MIR

- Low $NO_x$ "Full Surrogate" experiments more sensitive to $NO_x$ removal effects

Such experiments have been used to derive and evaluate mechanisms of ~60 types of VOCs for the SAPRC-99 reactivity scales

# LIMITATIONS OF ENVIRONMENTAL CHAMBER EXPERIMENTS FOR MECHANISM EVALUATION

- Very expensive to carry out (now $\geq$ $40K per VOC)

- Requires special expertise available at only a few laboratories

- Lower sensitivity to effects of oxidation products than predicted for the atmosphere

- Ambiguous mechanism evaluation data when more than one aspect of the mechanism is uncertain

- Not well suited for low volatility compounds

# MEASUREMENT OF
# DIRECT REACTIVITY

Direct reactivity is the effect of the VOC on $O_3$ formation directly due to its reactions or reactions of its products

One of the important factors affecting $O_3$ reactivity in the atmosphere

Often ambiguous to evaluate in environmental chamber reactivity experiments

- Radical initiation/inhibition effects can dominate results of High $NO_x$ experiments

- $NO_x$ removal effects can dominate results of low $NO_x$ experiments

- Errors in these indirect effects could mask (compensate for) errors in mechanism affecting direct reactivity in the atmosphere.

A direct reactivity measurement method could reduce the ambiguities in mechanism evaluation, especially for radical inhibiting VOCs

A direct reactivity measurement using a flow system may be more suitable to use with low volatility compounds than chamber experiments

# EXPERIMENTAL APPROACHES TO MEASURE DIRECT REACTIVITY

## Requirements

- Sensitive to NO $\rightarrow$ NO$_2$ conversion processes that are responsible for O$_3$ formation

- Both radicals and NO$_x$ in excess to reduce sensitivity to indirect effects

## HONO Photolysis System

- Large internal radical source and sink processes

- NO$_x$ present in excess

- Major reactions in absence of VOC result in consumption of HONO and formation of NO, NO$_2$, and HNO$_3$

- Addition of reactive VOC causes NO to NO$_2$ conversions that reduce NO levels and (if enough VOC is added) O$_3$ formation

- Effect of added VOC on $\Delta([O_3]\text{-}[NO])$ reflects the NO to NO$_2$ conversions caused by the added VOC, which is its direct reactivity.

# CHEMISTRY OF HONO
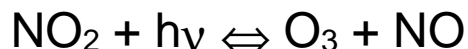# PHOTOLYSIS SYSTEM

## Reactions in the absence of added VOC

$$HONO + h\nu \rightarrow OH + NO$$
$$OH + HONO \rightarrow NO_2 + H_2O$$
$$OH + NO \rightarrow HONO$$
$$OH + NO_2 \rightarrow HNO_3$$
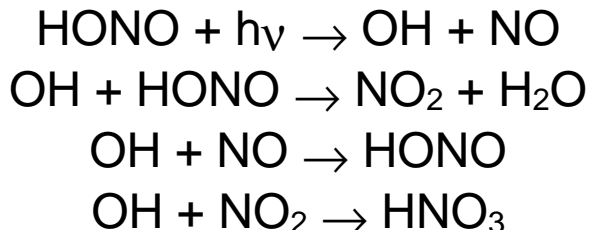
Net effect is formation of NO, $NO_2$ and $HNO_3$.

Additional reactions in presence of VOC

$$VOC + OH \rightarrow - \alpha \, NO + \text{other products}$$

Net effect is lower NO formation and (if enough VOC is added) formation of $O_3$ through reactions

$$NO_2 + h\nu \Leftrightarrow O_3 + NO$$

## For low amount of added VOC:

$$\frac{([O_3]-[NO])_{VOC} - ([O_3]-[NO])_{no\,VOC}}{[VOC\,added]}$$

is approximately proportional to

$$kOH(VOC) \times NO \text{ conversions per VOC reacted}$$

## Therefore, $\Delta([O_3]-[NO]) / [VOC]$ provides a measure of the VOC's direct reactivity

# EXAMPLE OF ENVIRONMENTAL CHAMBER IRRADIATIONS OF HONO – AIR AND HONO – VOC – AIR MIXTURES

## HONO ONLY



Concentration (ppm) vs Irradiation Time (minutes)
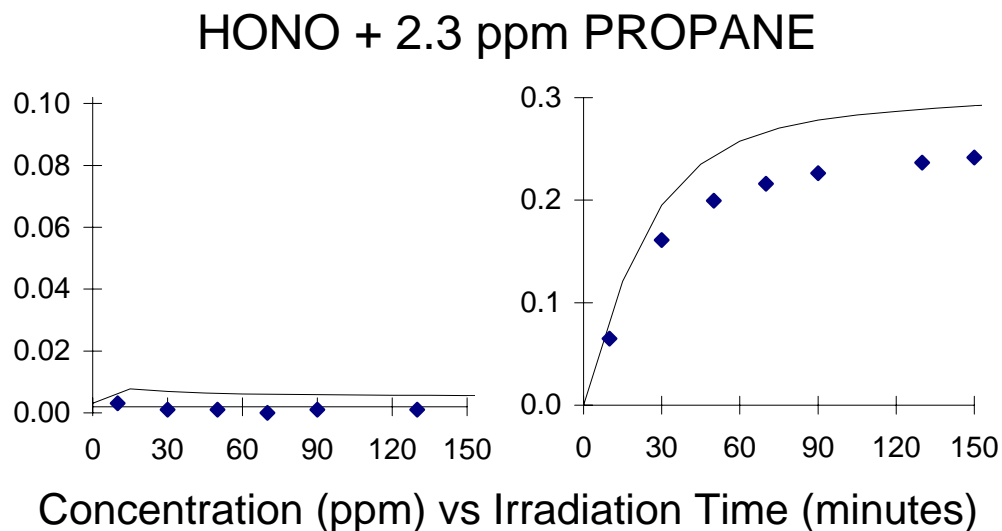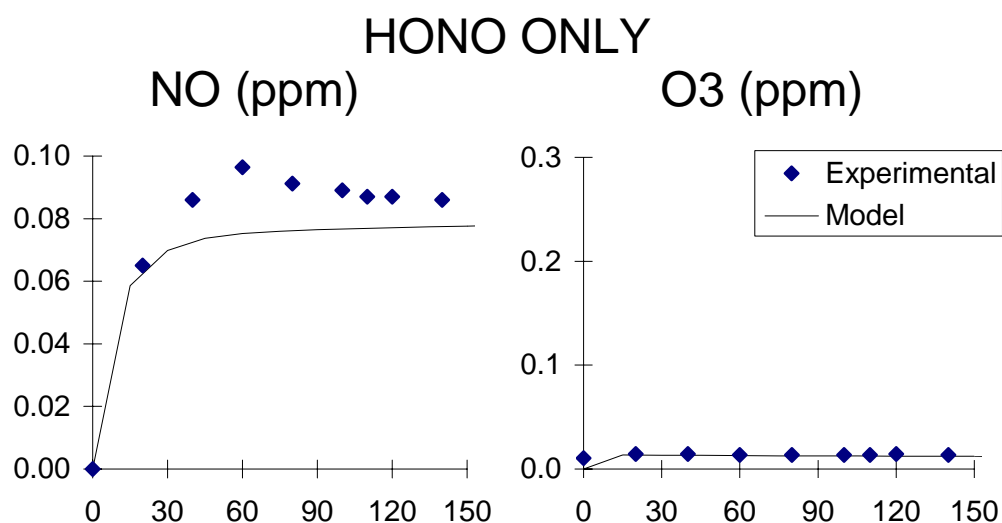
Runs DTC686A and B
Initial HONO $\approx$ 0.35 ppm
$NO_2$ photolysis rate $\approx$ 0.17 $min^{-1}$, Blacklight irradiation

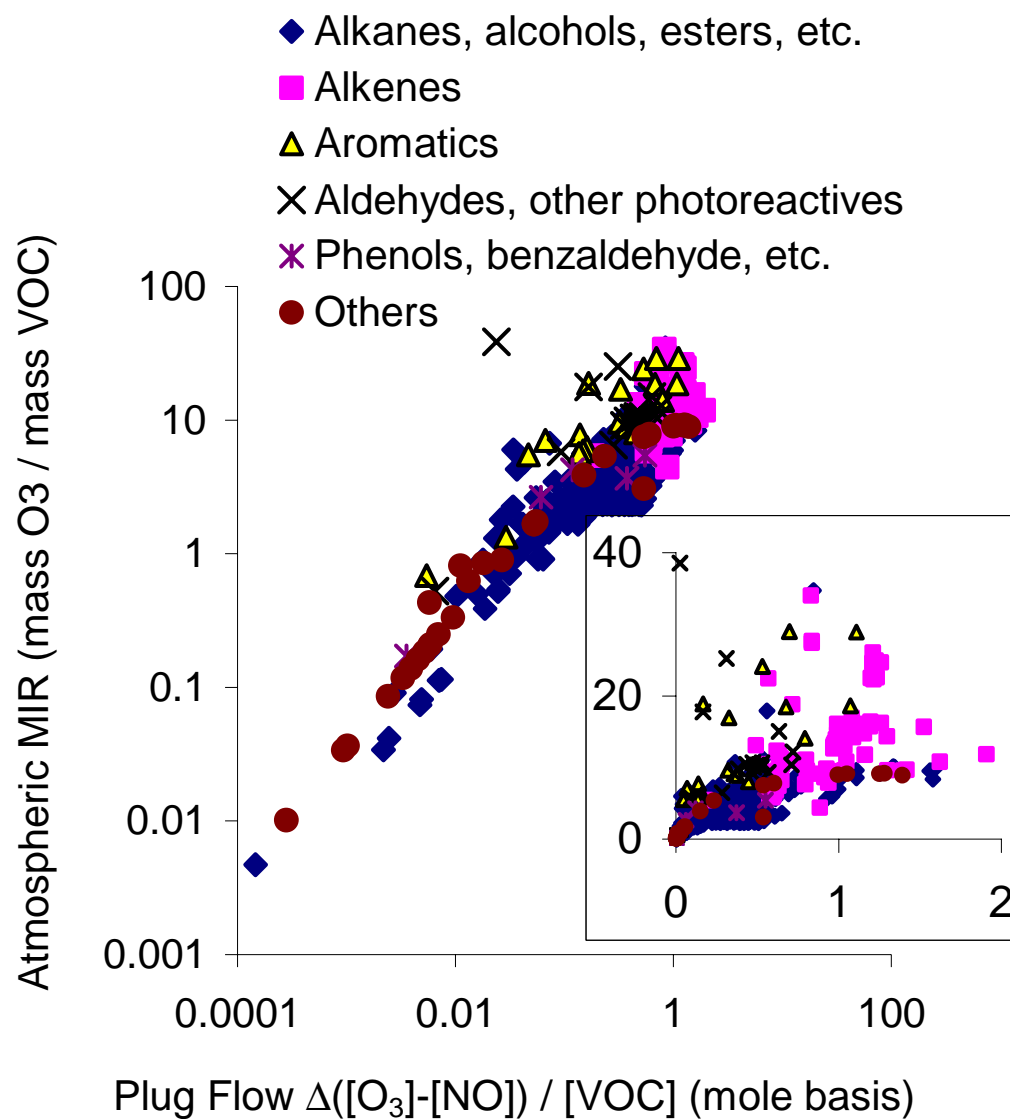# CALCULATED SENSITIVITIES OF EXPERIMENTS OR SIMULATIONS TO VARIOUS MECHANISM COMPONENTS

| Type of Experiment or Simulation | Mechanistic Reactivity of Mechanism Component (mol $O_3$ / mol VOC reacted) | | |
|---|---|---|---|
| | NO to $NO_2$ Convert. | Pure Radical Source | Ketone Product Form. |
| <u>HONO + VOC Experiment</u> | | | |
| Stirred Flow | 0.7 | 0.32 | 1.7 |
| Plug Flow | 0.9 | 0.12 | 0.14 |
| <u>Environmental Chamber Reactivity Experiment</u> | | | |
| Mini-Surrogate | 0.6 | 6.0 | 0.16 |
| High $NO_x$ Surg. | 0.6 | 3.0 | 0.33 |
| Low $NO_x$ Surg. | 0.4 | -0.3 | 0.09 |
| <u>Atmospheric Reactivity Simulation</u> | | | |
| MIR | 0.6 | 2.4 | 4.1 |
| EBIR | 0.4 | 1.1 | 1.4 |

# CORRESPONDENCE BETWEEN K(OH) AND DIRECT REACTIVITY MEASURED BY A HONO PHOTOLYSIS SYSTEM
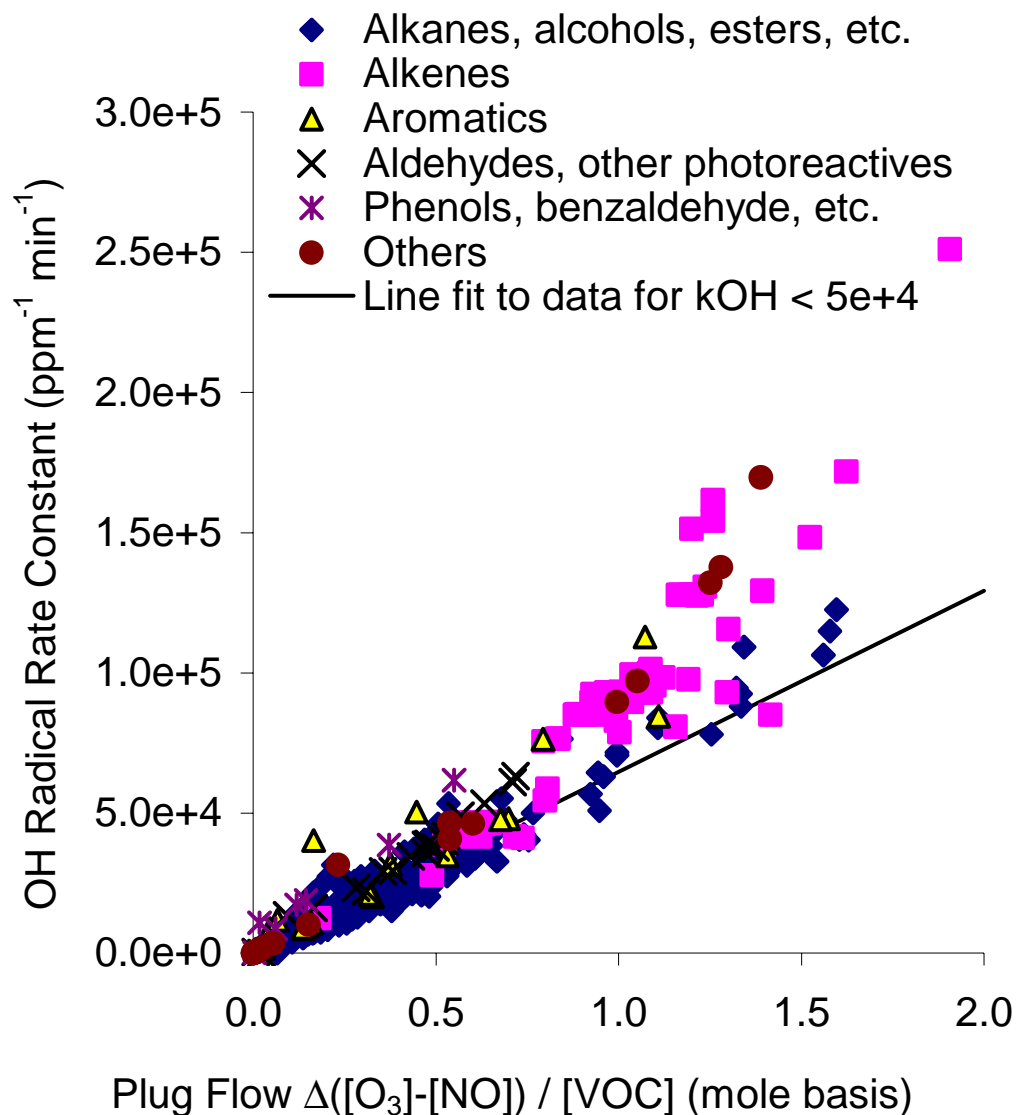


PLOT SHOWS SAPRC-99 PREDICTIONS OF PLUG FLOW HONO + VOC EXPERIMENTS

CORRESPONDENCE BETWEEN MIR AND DIRECT REACTIVITY MEASURED BY A HONO PHOTOLYSIS SYSTEM

Legend:
- Alkanes, alcohols, esters, etc.
- Alkenes
- Aromatics
- Aldehydes, other photoreactives
- Phenols, benzaldehyde, etc.
- Others

Y-axis: Atmospheric MIR (mass O3 / mass VOC)

X-axis: Plug Flow $\Delta([O_3]-[NO]) / [VOC]$ (mole basis)

PLOT SHOWS SAPRC-99 PREDICTIONS OF PLUG FLOW HONO + VOC EXPERIMENTS

# HONO GENERATION SYSTEM USED
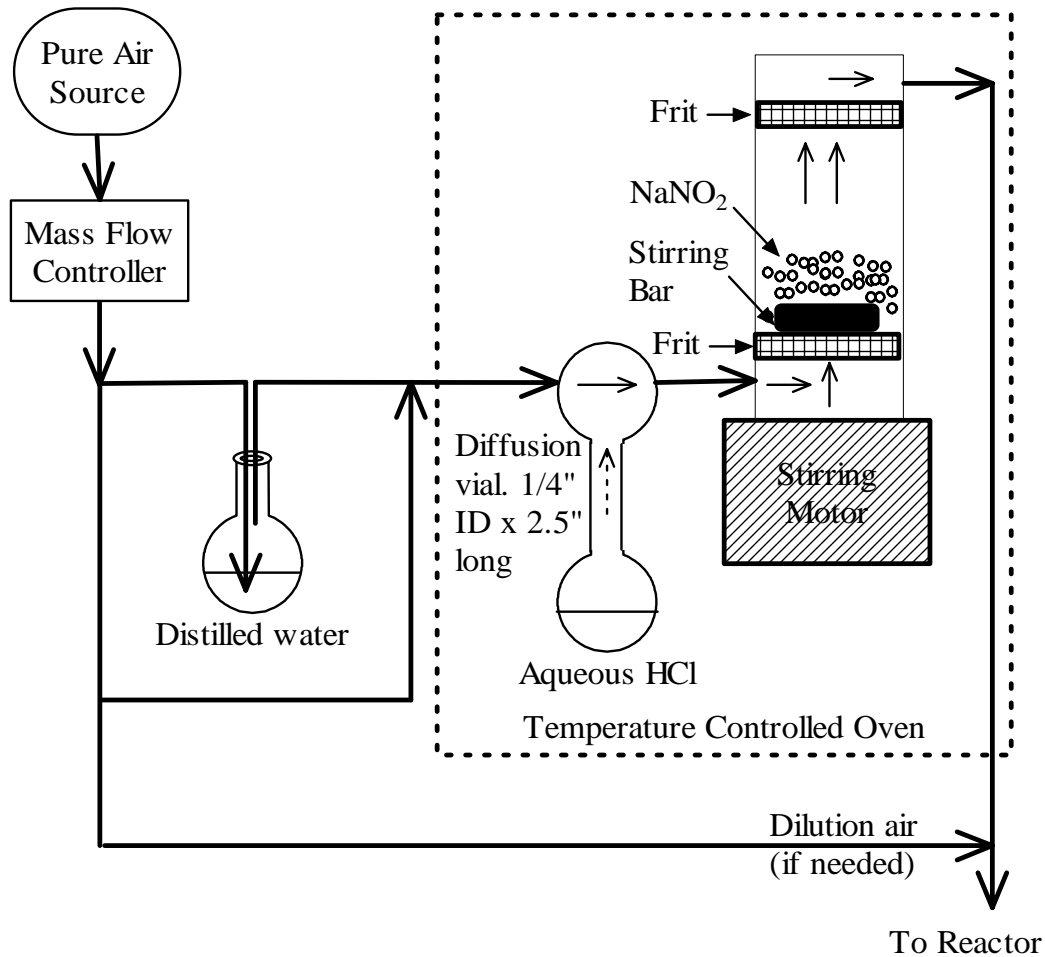


- Based on method of Febo et al (1995)

- Formed via $HCl + NaNO_2 \rightarrow NaCl + HONO$

- Produces HONO output of $\geq \sim 0.2$ millimole /min ($\geq \sim 5$ ppm in air at 1 liter/minute)

- No measurable HCl at this output level. HONO purity of ~90% (~5% each NO, $NO_2$).

# PHOTOGRAPH OF HONO
# GENERATION SYSTEM
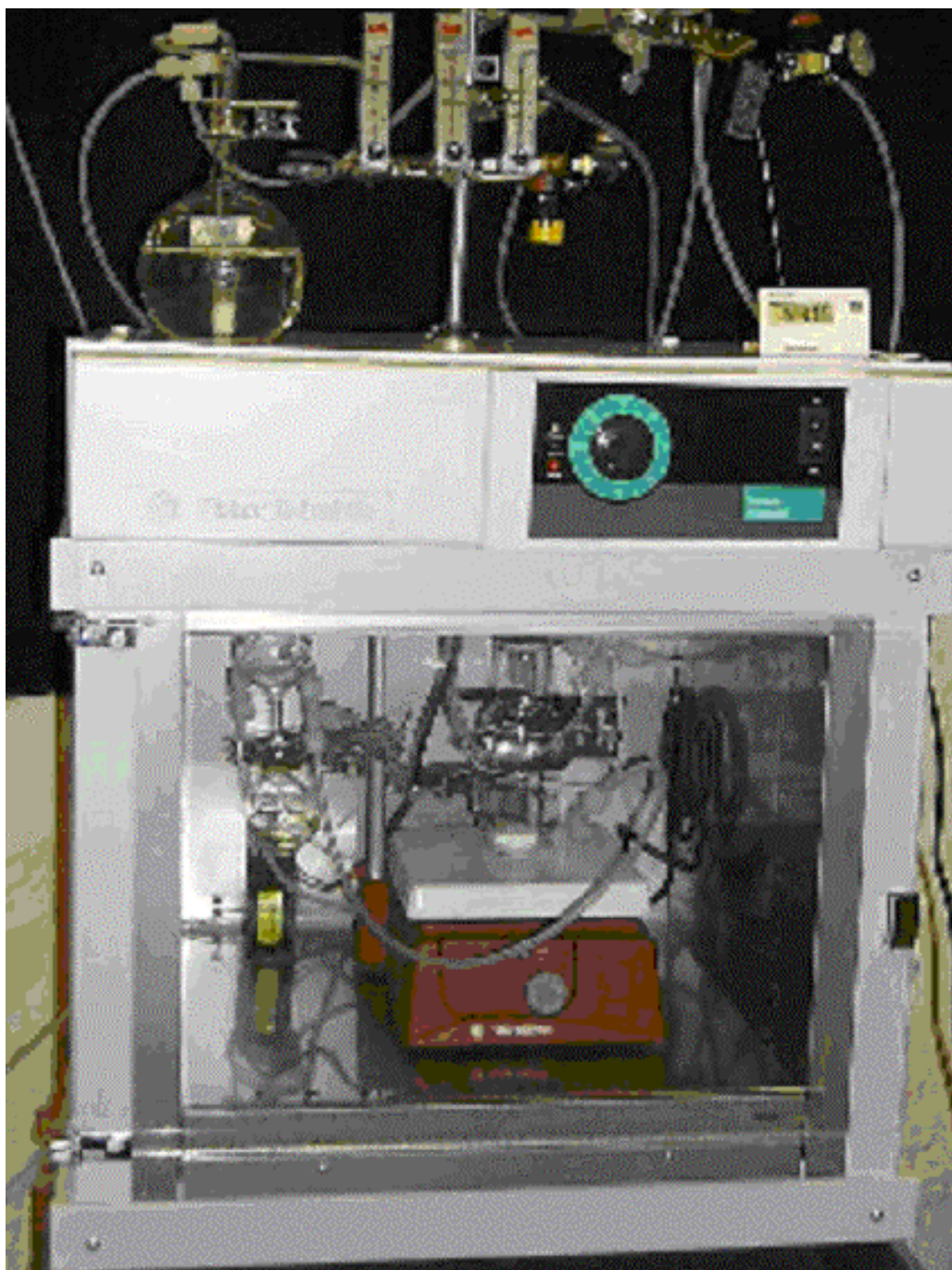
# ALTERNATIVE EXPERIMENTAL APPROACHES FOR HONO – VOC REACTION SYSTEM

## Static System

Irradiation of HONO and HONO + VOC in a static reactor or environmental chamber

Advantages:

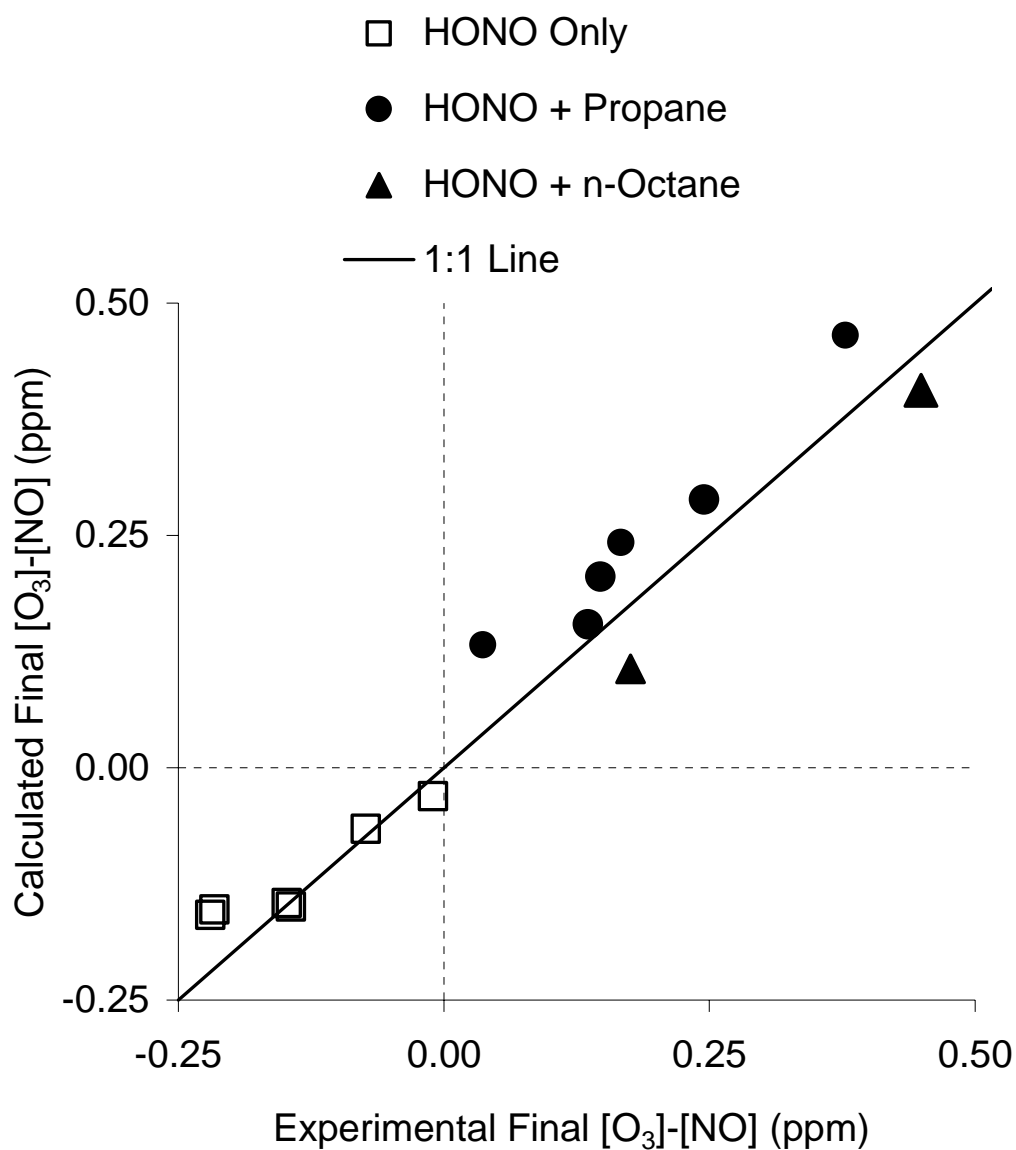- Simplest to characterize for modeling

Disadvantages:

- Difficult to reproduce conditions from run to run

- Time consuming to carry out

- Not well suited for low volatility compounds

Because of its disadvantages, only a limited number of static experiments were conducted to evaluate ability to model HONO chemistry

Results of experiments were generally consistent with model predictions, but there was some run-to-run variability

**EXPERIMENTAL VS CALCULATED [O$_3$]-[NO] FOR THE STATIC HONO + VOC IRRADIATIONS**

□ HONO Only
● HONO + Propane
▲ HONO + n-Octane
—— 1:1 Line

Calculated Final [O$_3$]-[NO] (ppm)

Experimental Final [O$_3$]-[NO] (ppm)

# ALTERNATIVE EXPERIMENTAL APPROACHES (CONT'D)

## Continuous Flow Systems

HONO or HONO + VOC mixtures are continuously flowed through an irradiated reactor with the output sampled.

Can be carried out in stirred flow or plug flow modes

Advantages

- Easily interfaced to HONO generation system, which produces continuous output

- Continuous VOC injection potentially better suited to low volatility compounds

- Potentially able to obtain more data points per unit time than static methods

- Potential to develop self-contained system that can be used to conduct experiments at lower cost and effort

Disadvantages

- Dynamic systems more uncertain to model

- Uses lower volume reactors where surface absorption effects may be more important

# ANALYTICAL METHODS EMPLOYED

## Chemiluminescence NO - NO$_x$ Analyzer

- Needed to determine $\Delta([O_3]\text{-}[NO])$ caused by added VOC and to determine level of NO impurity in HONO

- "NO$_2$" channel gives 100% response to HONO, so can be used to determine HONO input

## O$_3$ Analyzer

- Needed to determine $\Delta([O_3]\text{-}[NO])$ with high added VOC

## Specific NO$_2$ Analysis (by TDLAS)

- TDLAS or GC-Luminol used periodically to determine level of NO$_2$ impurity in HONO input

- NO and NO$_2$ impurity levels found to be similar.

- Not normally used or needed for experiments

## GC Analysis of Test VOC

- Needed to determine amount of VOC added

- Most labor intensive aspect of most experiments

- Problems with data precision for low volatility VOCs

# FIRST SERIES:
# STIRRED FLOW EXPERIMENTS

Stirred flow method involves use of a reactor that can be assumed to be well mixed

Modeled Assuming

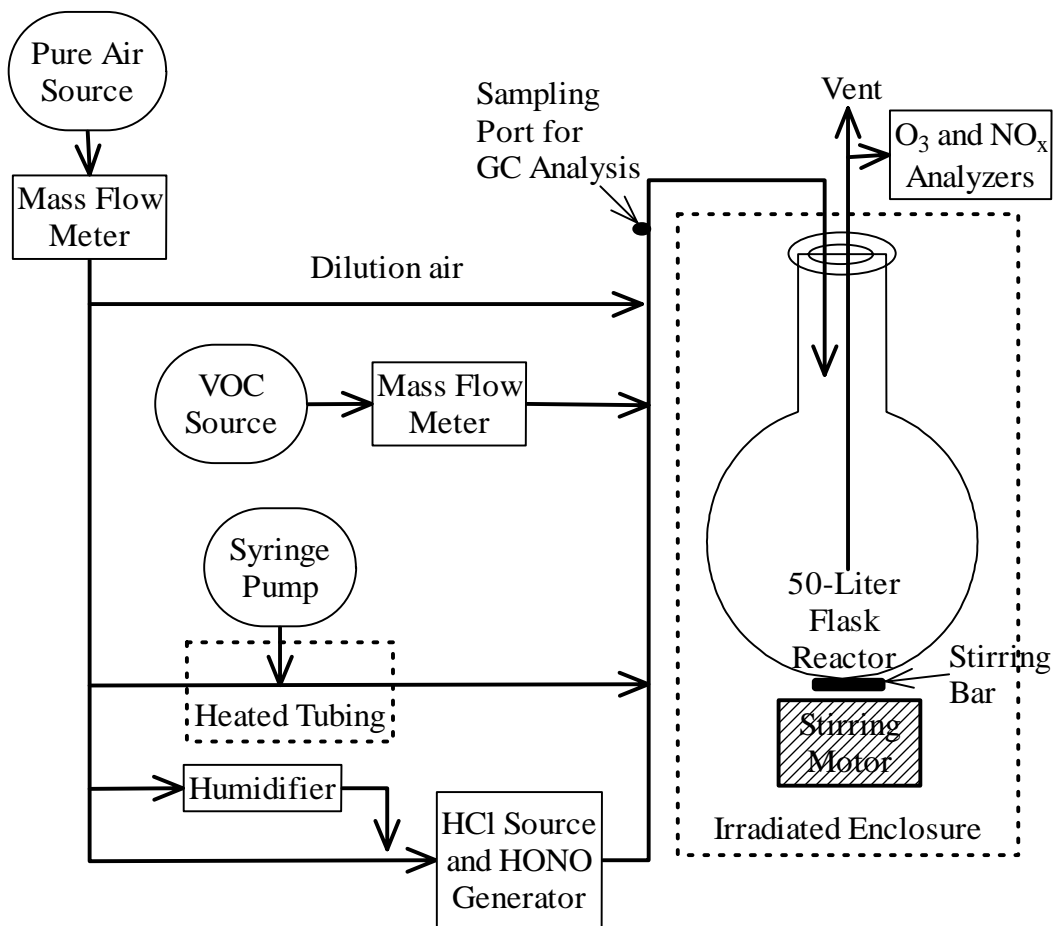$$d[C]_t/dt = ([C]_0 - [C]_t) \, (F \, / \, V) + ChemTrans(C,t)$$

Where

- $[C]_0$ = concentration entering the reactor
- $[C]_t$ = concentration in the mixed reactor
- $F$ = flow
- $V$ = reactor volume
- $ChemTrans(C,t)$ = chemical reaction rates

Employed in first series of experiments because design allows for longer reaction times, to give larger $\Delta([O3]-[NO])$ changes with added VOCs.
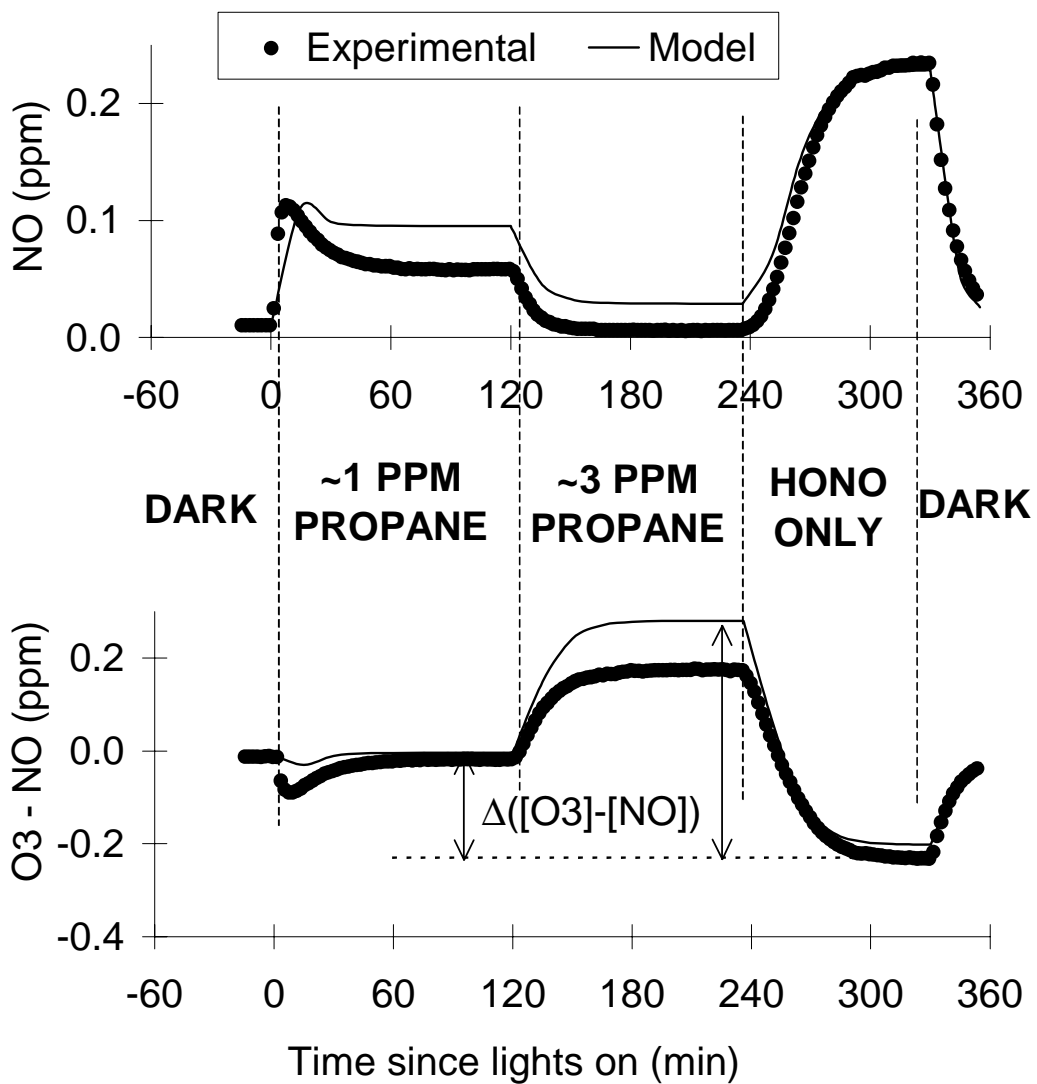
Conditions:

- 50-liter unstirred or stirred Pyrex carboy or 50-liter stirred Pyrex flask used as reactor

- Typical reactor flow: ~5 liter/minute.

- Typical initial HONO ~0.7 ppm

- Irradiated in blacklight chamber enclosure with $NO_2$ photolysis rate of ~1.1 min$^{-1}$.

# EXAMPLE LAYOUT OF
# STIRRED FLOW SYSTEM

Pure Air Source

Mass Flow Meter

Sampling Port for GC Analysis

Dilution air

Vent

$O_3$ and $NO_x$ Analyzers

VOC Source

Mass Flow Meter

Syringe Pump

Heated Tubing

50-Liter Flask Reactor

Stirring Bar

Humidifier

HCl Source and HONO Generator

Stirring Motor

Irradiated Enclosure

# EXAMPLE OF STIRRED FLOW
# EXPERIMENT RESULTS

# RESULTS OF PROPANE EXPERIMENTS
# IN STIRRED FLOW REACTORS

◆ Unstirred Carboy

■ Stirred Carboy

△ Stirred Flask

— Model

$\Delta([O_3]-[NO])$ vs Added VOC (ppm)
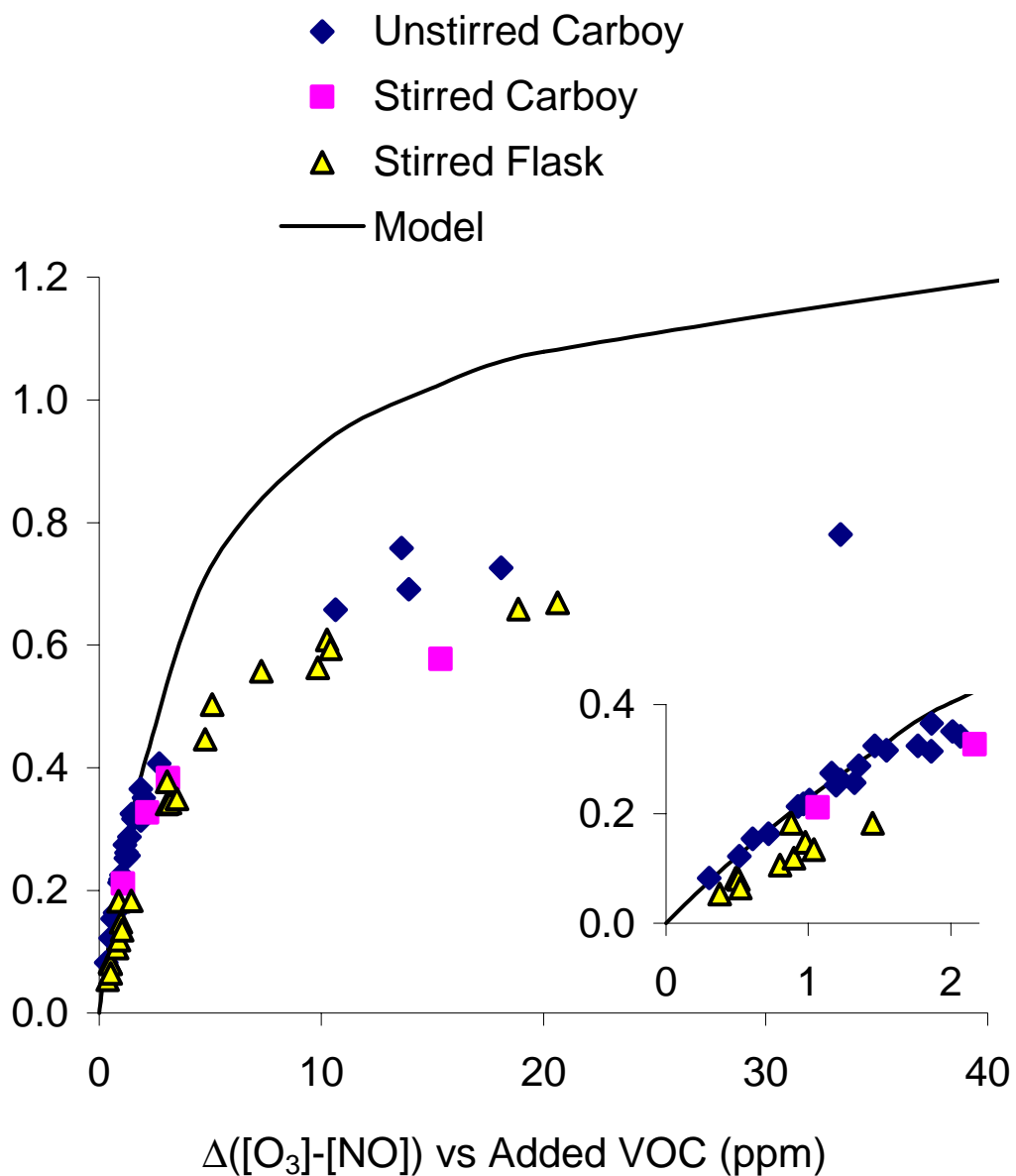
# N-OCTANE AND N-DODECANE STIRRED-FLOW EXPERIMENTS
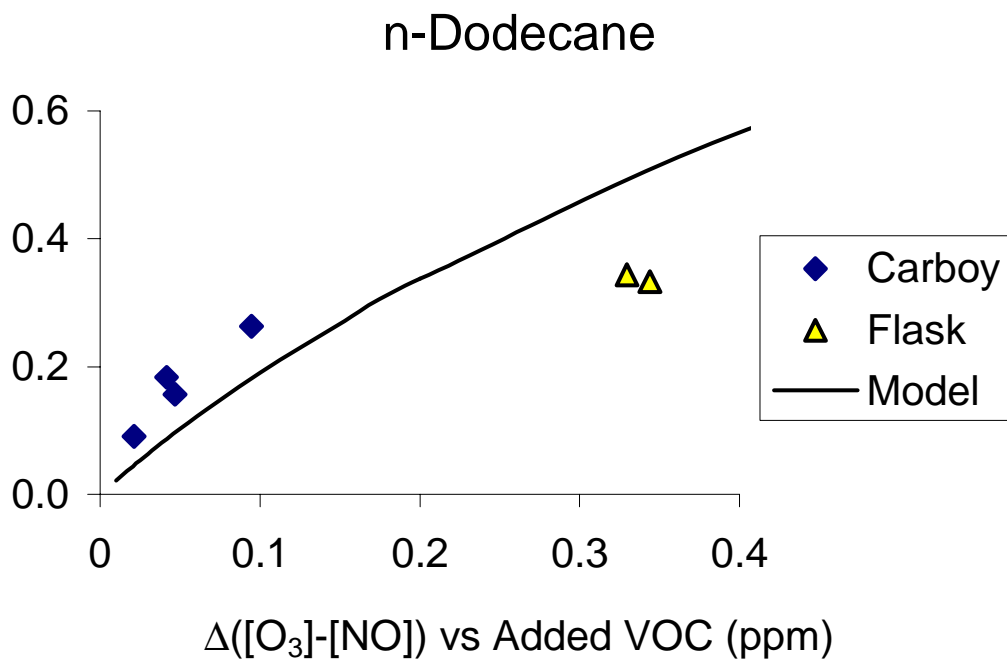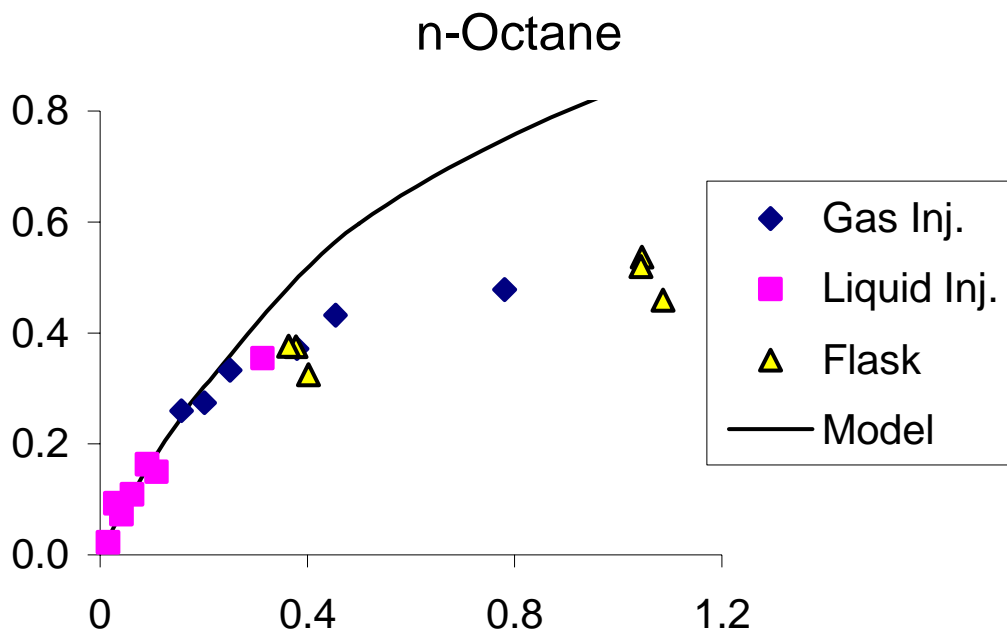
# SUMMARY OF DIRECT REACTIVITY RESULTS USING STIRRED FLOW SYSTEM

| Compound | Low Concentration Limit $\Delta([O_3]-[NO]) / [VOC]$ (molar basis) | | |
|---|---|---|---|
| | Experimental | Calculated | Model Bias |
| Propane | 0.30 | 0.26 | -14% |
| n-Butane | 0.73 | 0.70 | -5% |
| n-Hexane | 1.55 | 1.56 | 0% |
| n-Octane | 2.15 | 1.83 | -15% |
| n-Decane | 3.16 | 2.05 | -35% |
| n-Dodecane | 5.24 | 2.17 | -59% |
| CO | 0.025 | 0.020 | -20% |
| Acetone | 0.109 | 0.080 | -27% |

## Problems with Stirred Flow Results

- Consistent model underprediction of $\Delta([O_3]-[NO])$ at high added VOC

- Higher than expected effect of molecule size on direct reactivities of homologous n-alkanes cannot be explained.

# SECOND AND THIRD SERIES:
# PLUG FLOW EXPERIMENTS

Plug flow method involves use of a tube-shaped reactor where it is assumed that mixing in the direction of the flow is negligible
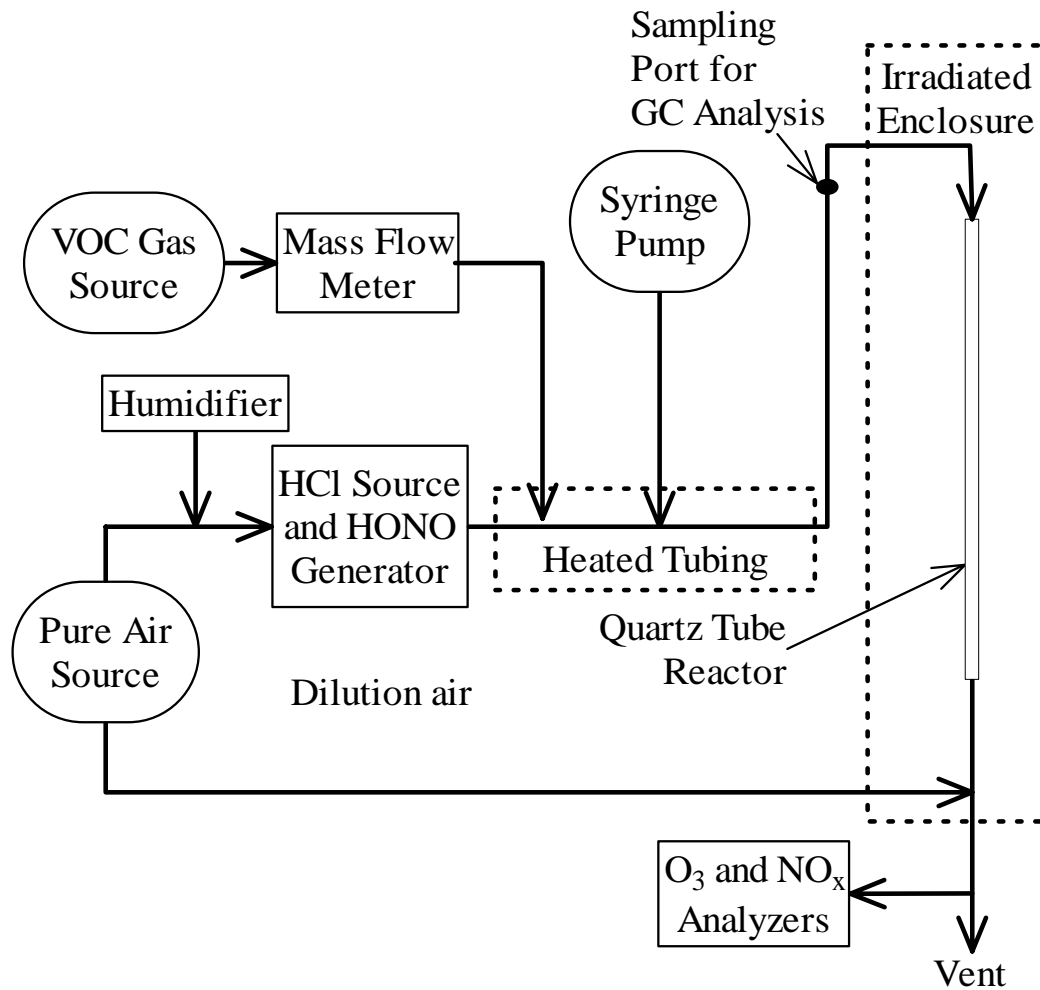
Modeled as a static system with reaction time given by the volume divided by the flow rate

Examined as an alternative approach because of inconsistency with results of stirred flow system with model predictions
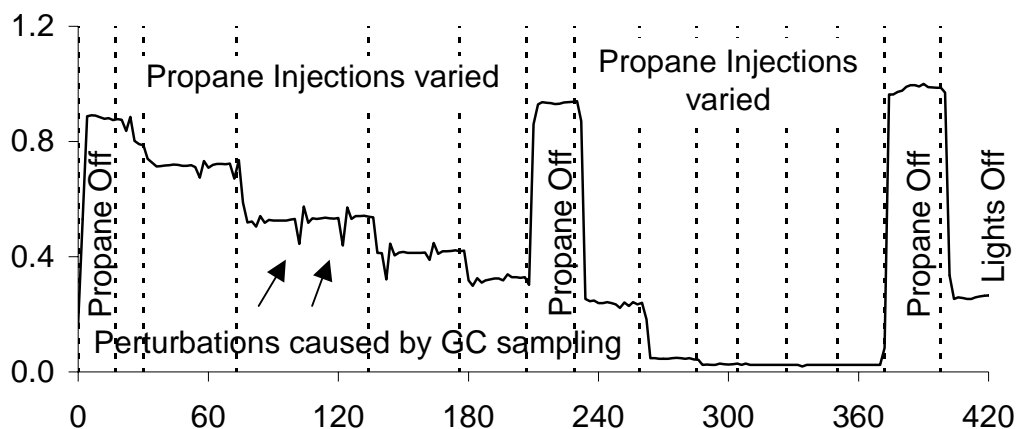
Two series of experiments carried out:

| Condition | First Series | Second Series |
|---|---|---|
| Reactor | 29 m x 0.75 cm ID PFA Teflon Tube (1.3 liters) | 86 cm x 1.8 cm ID quartz tube (0.283 liters) |
| Flow | ~1 liter/minute | 0.5 liter/minute |
| Rxn Time | 1.3 min. | 0.6 min. |
| HONO | ~3.3 ppm | ~4 ppm |
| Lights | Blacklights | Blacklights |
| $k_{PHOT}(NO_2)$ | ~0.6 - 1 min$^{-1}$ | 0.6 min$^{-1}$ |

# EXAMPLE LAYOUT OF PLUG FLOW SYSTEM (WITH QUARTZ TUBE)

Sampling
Port for
GC Analysis

Irradiated
Enclosure

VOC Gas
Source

Mass Flow
Meter

Syringe
Pump

Humidifier

HCl Source
and HONO
Generator

Heated Tubing

Pure Air
Source

Dilution air
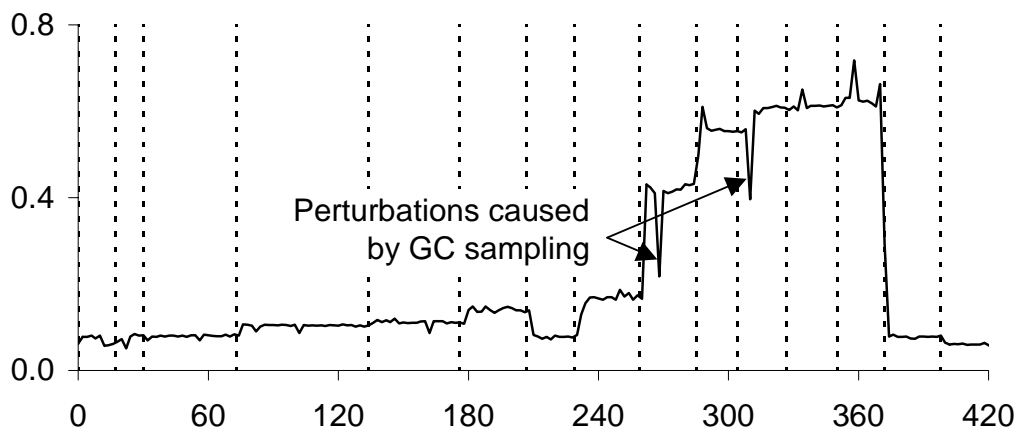
Quartz Tube
Reactor

$O_3$ and $NO_x$
Analyzers

Vent

# EXAMPLE DATA WITH PLUG FLOW SYSTEM (29 M PFA TUBE): PROPANE EXPERIMENT

## NO (ppm)



Propane Injections varied

Propane Injections varied

Propane Off

Propane Off

Propane Off

Lights Off

Perturbations caused by GC sampling
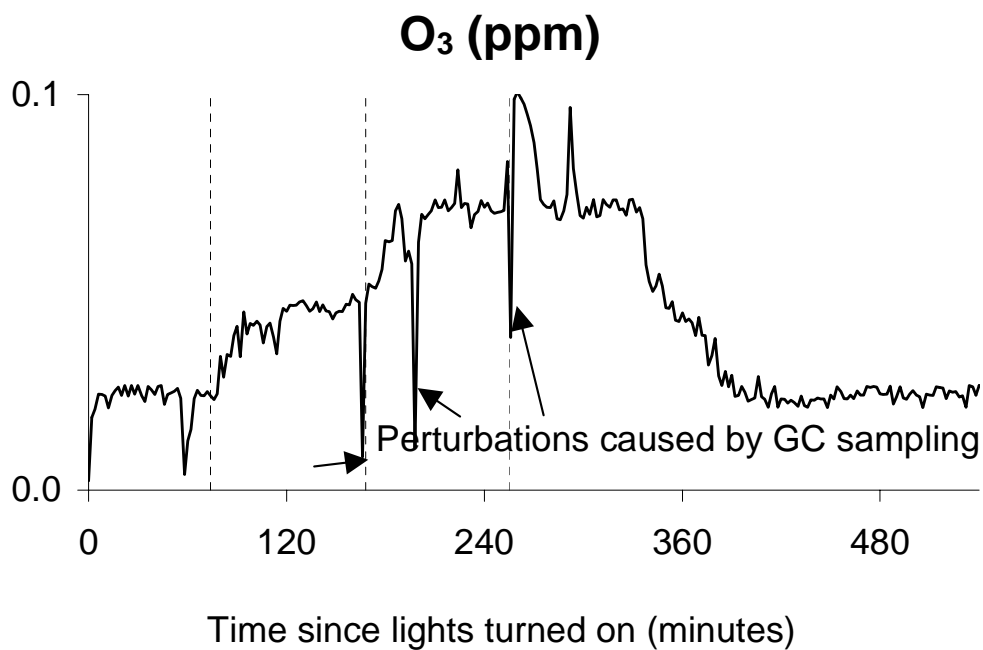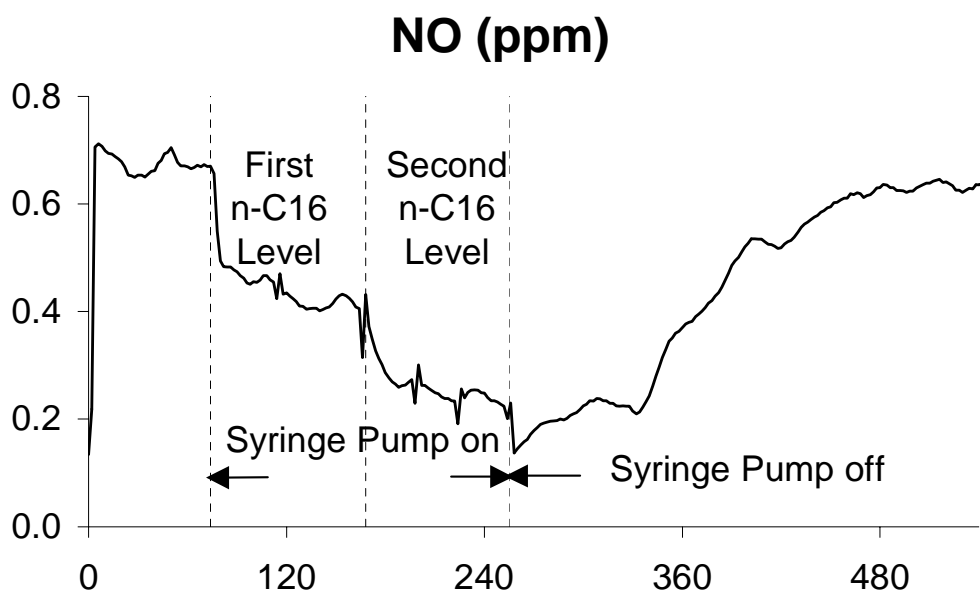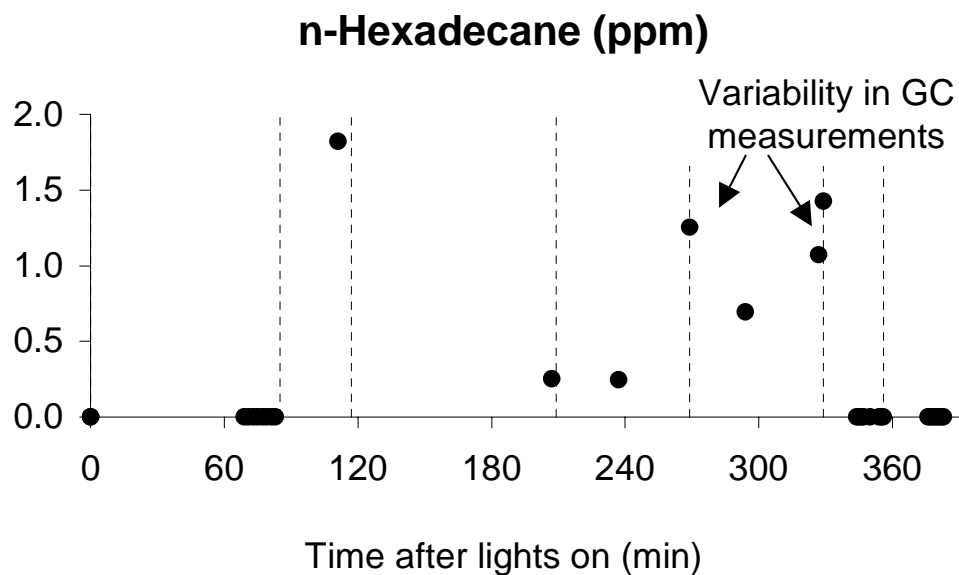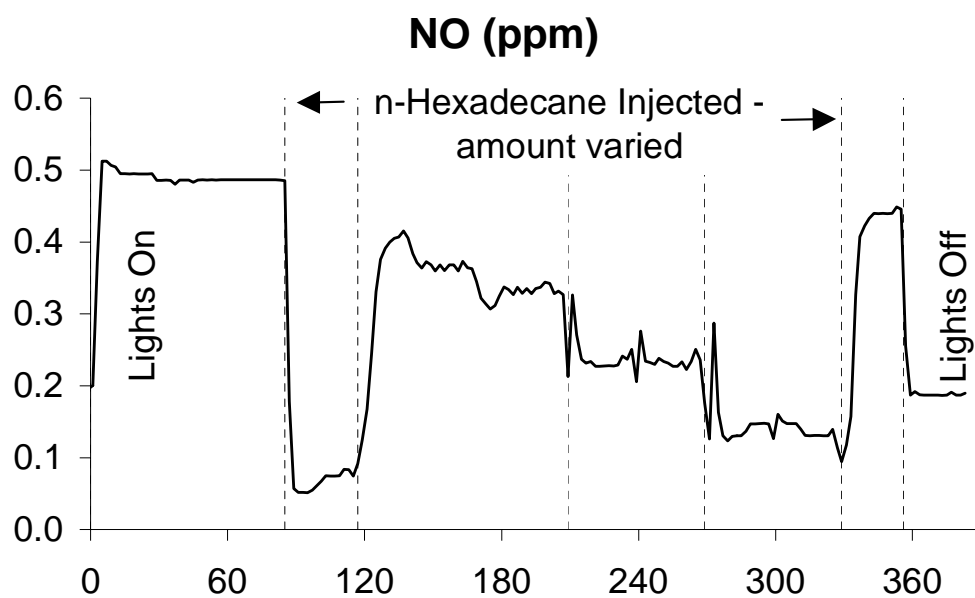
## O$_3$ (ppm)



Perturbations caused by GC sampling

Time since lights turned on (minutes)

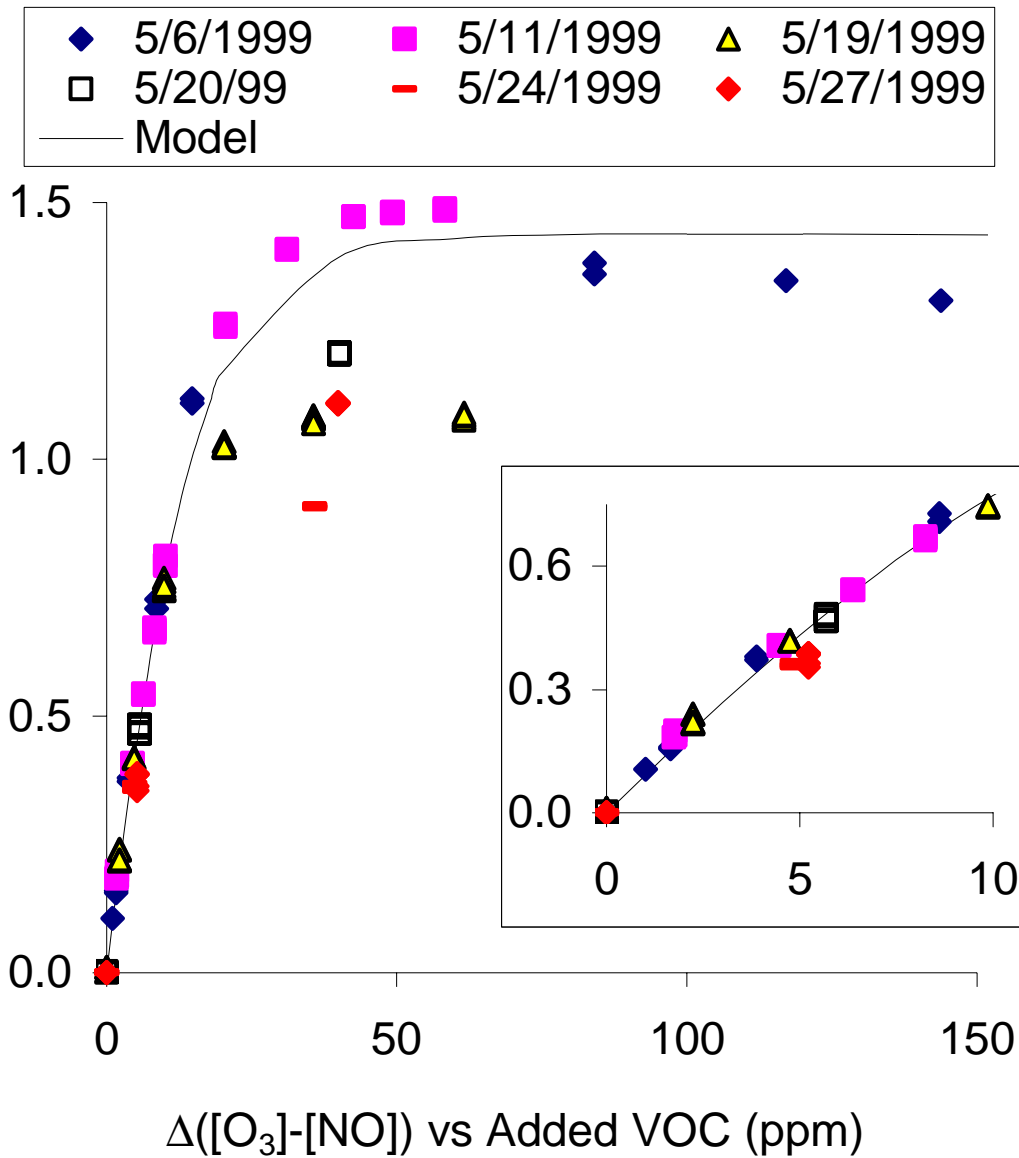# EXAMPLE DATA WITH PLUG FLOW SYSTEM (29 M PFA TUBE): N-HEXADECANE EXPERIMENT

## NO (ppm)



First n-C16 Level

Second n-C16 Level

Syringe Pump on

Syringe Pump off

## O₃ (ppm)



Perturbations caused by GC sampling

Time since lights turned on (minutes)

# EXAMPLE DATA WITH PLUG FLOW SYSTEM (86 CM QUARTZ TUBE): N-HEXADECANE EXPERIMENT

## NO (ppm)



n-Hexadecane Injected - amount varied

Lights On

Lights Off

## n-Hexadecane (ppm)



Variability in GC measurements

Time after lights on (min)

# EXAMPLE RESULTS OF PLUG FLOW EXPERIMENTS WITH 29M PFA TUBE

## PROPANE

Legend:
- ◆ 5/6/1999
- ■ 5/11/1999
- △ 5/19/1999
- □ 5/20/99
- ▬ 5/24/1999
- ◆ 5/27/1999
- — Model

$\Delta([O_3]-[NO])$ vs Added VOC (ppm)

**EXAMPLE RESULTS OF PLUG FLOW EXPERIMENTS WITH 29M PFA TUBE**
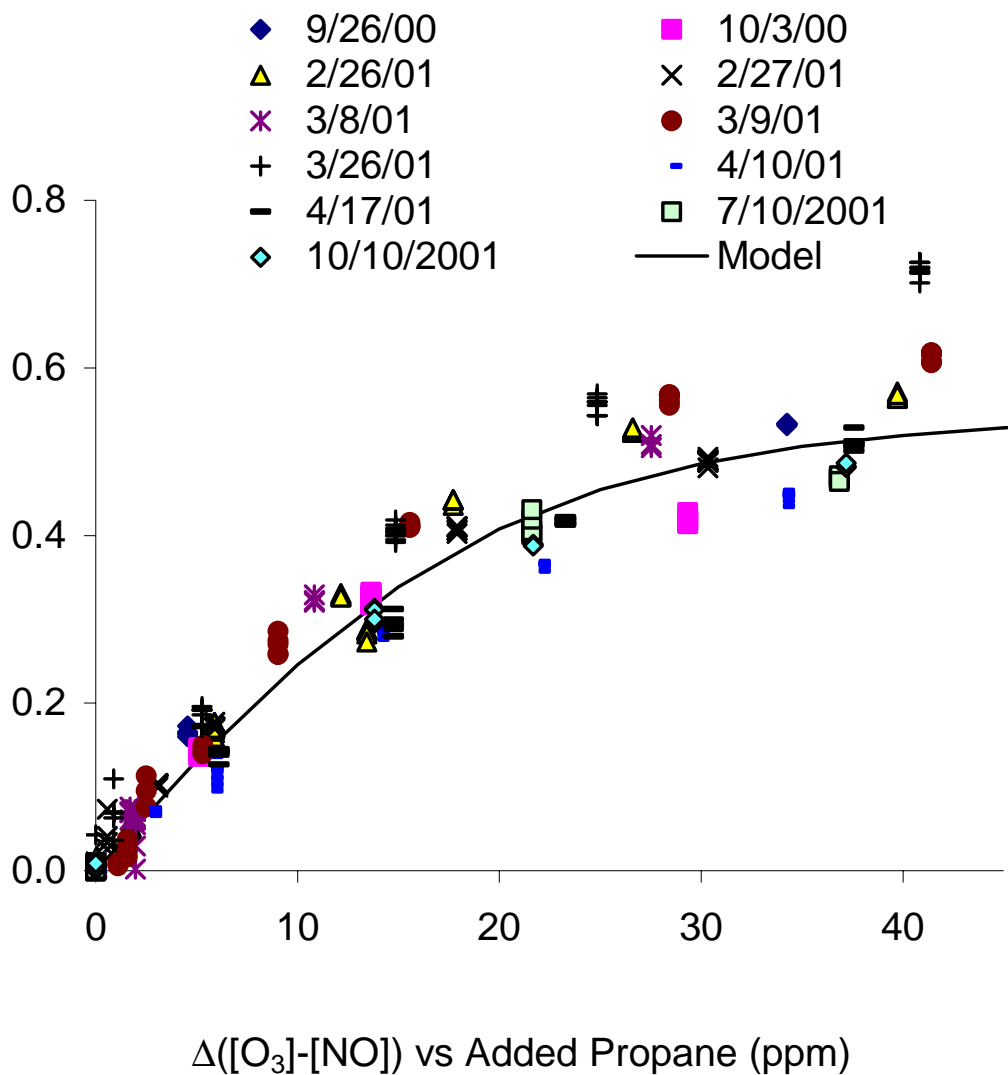
**n-Dodecane through n-Hexadecane**
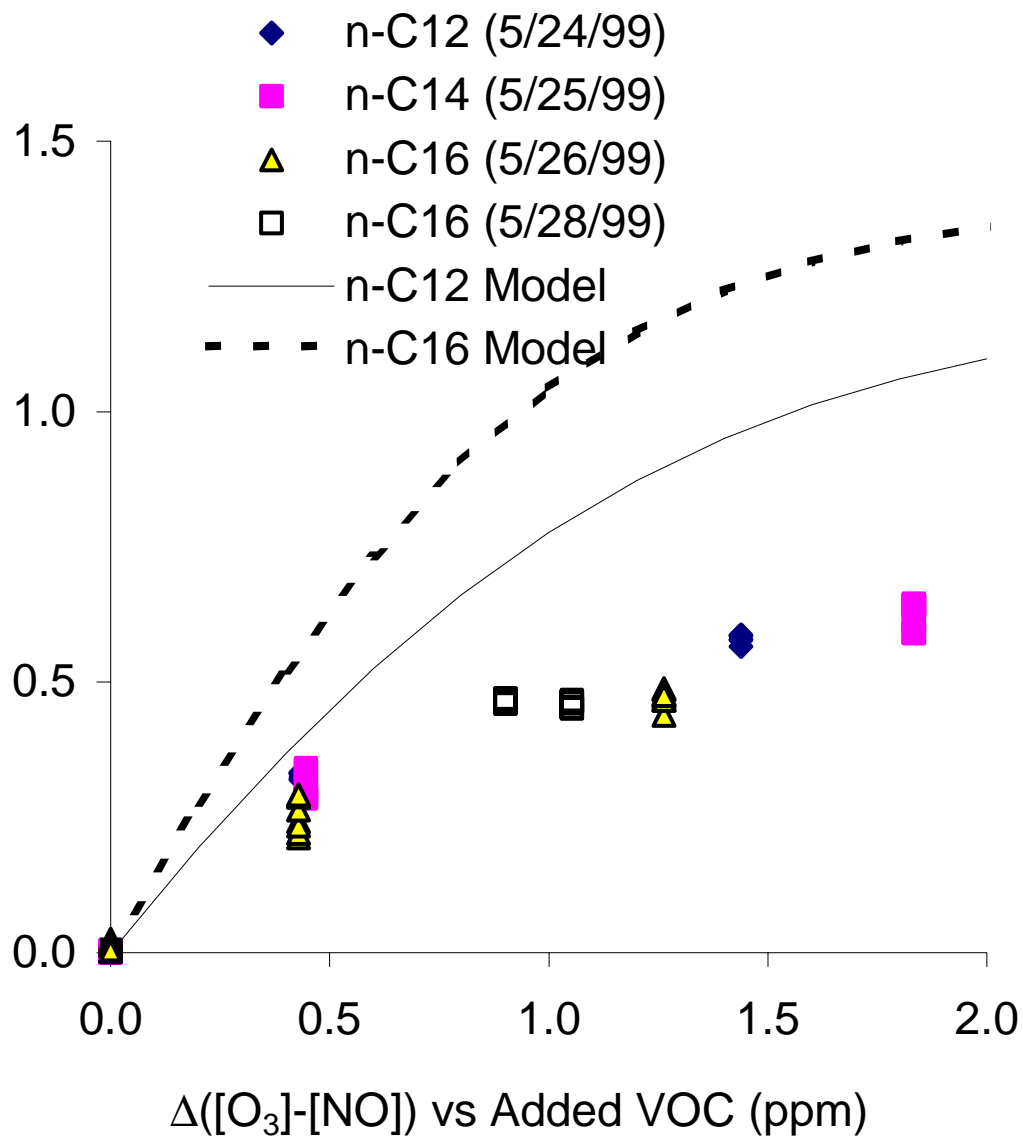
## SUMMARY OF DIRECT REACTIVITY RESULTS USING THE 29 M PFA TUBE PLUG FLOW SYSTEM

| Compound | Low Concentration Limit $\Delta([O_3]-[NO]) / [VOC]$ | | |
| --- | --- | --- | --- |
| | Measured | Calculated | Model Bias |
| Propane | 0.10 | 0.11 | 9% |
| n-Octane | 0.99 | 0.90 | -9% |
| n-Decane | 1.65 | 1.01 | -39% |
| n-Dodecane | 1.06 | 1.07 | 1% |
| n-Tetradecane | 0.90 | 1.39 | 55% |
| n-Hexadecane | 0.81 | 1.58 | 95% |
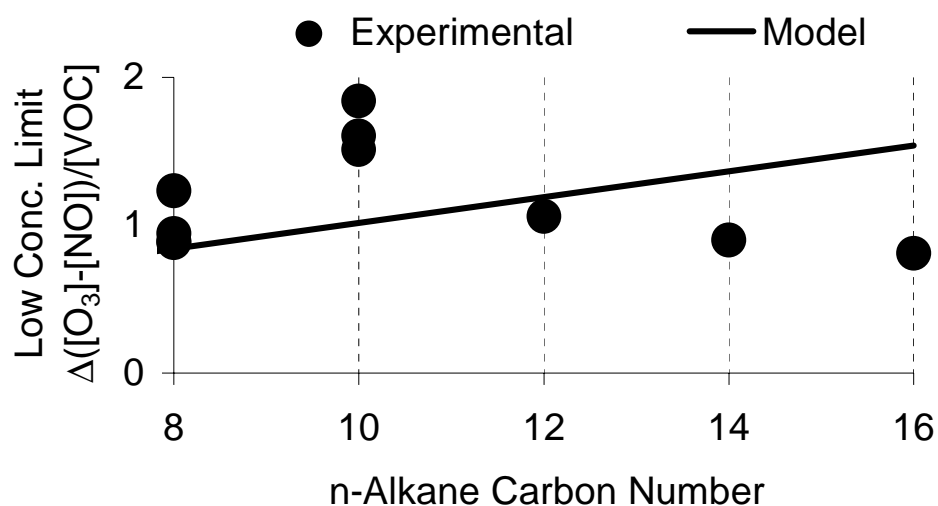
# EXAMPLE RESULTS OF PLUG FLOW EXPERIMENTS WITH QUARTZ TUBE

## PROPANE



$\Delta([O_3]-[NO])$ vs Added Propane (ppm)

# EXAMPLE RESULTS OF PLUG FLOW EXPERIMENTS WITH QUARTZ TUBE

## n-C$_{13}$ and n-C$_{14}$



Legend:
- ◆ 10/19/00 (n-C13)
- ■ 10/5/00 (n-C14)
- —— n-C13 Model
- - - - n-C14 Model

## n-C$_{16}$



Legend:
- ◆ 36795
- ■ 9/27/00
- —— Model

$\Delta([O_3]-[NO])$ vs Added VOC (ppm)
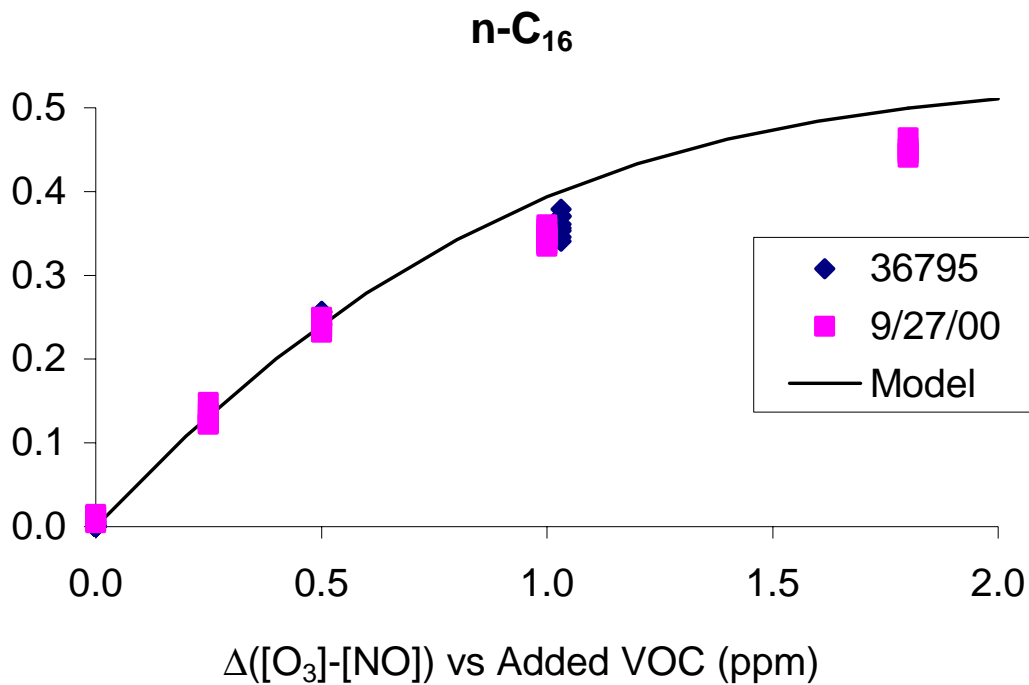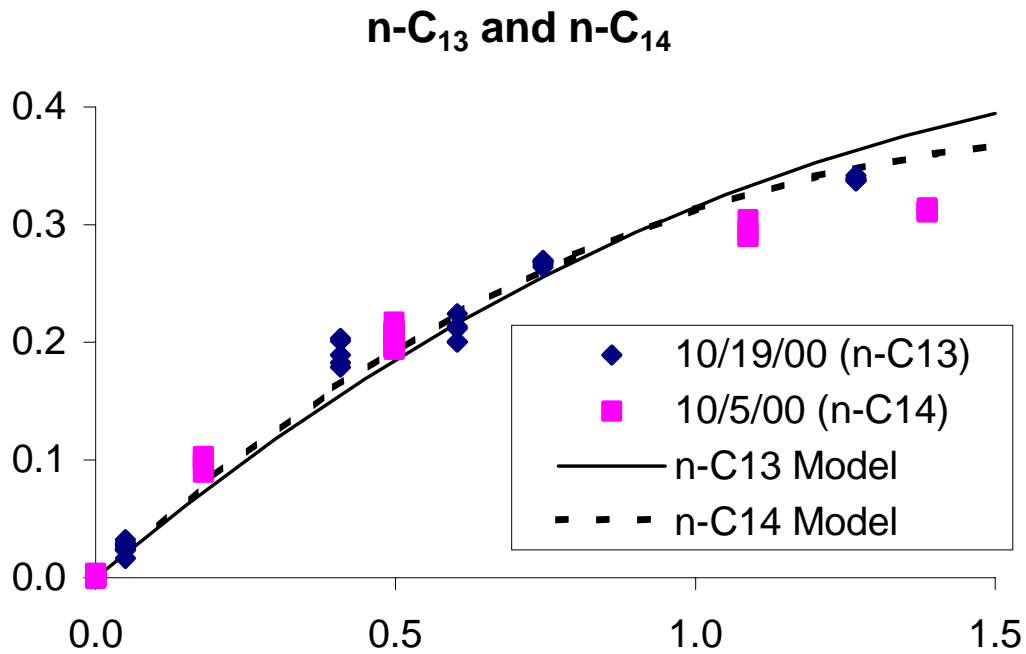
# RESULTS OF QUARTZ TUBE PLUG FLOW EXPERIMENTS FOR THE HOMOLOGOUS N-ALKANES



Low Concentration Limit
$\Delta([O_3]-[NO]) / [VOC]$
vs. Carbon Number

● Experimental
— Calculated
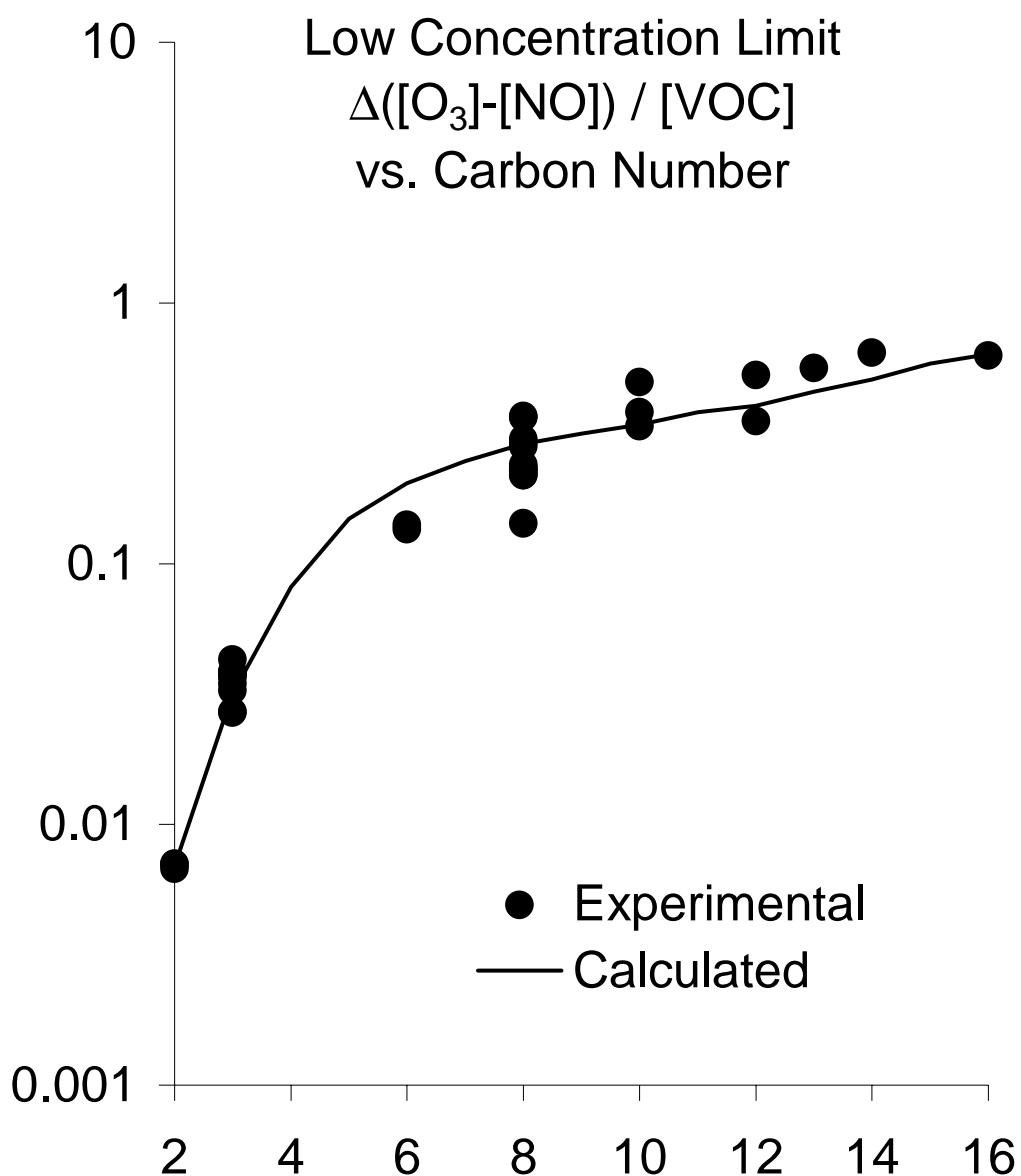
# MODEL PERFORMANCE IN SIMULATING
# PLUG FLOW QUARTZ TUBE DATA
# FOR ALL COMPOUNDS STUDIED

**Low Conc. Limit D([O3]-[NO]) / [VOC]
(Calculated) - (Experimental) / (Calculated)**
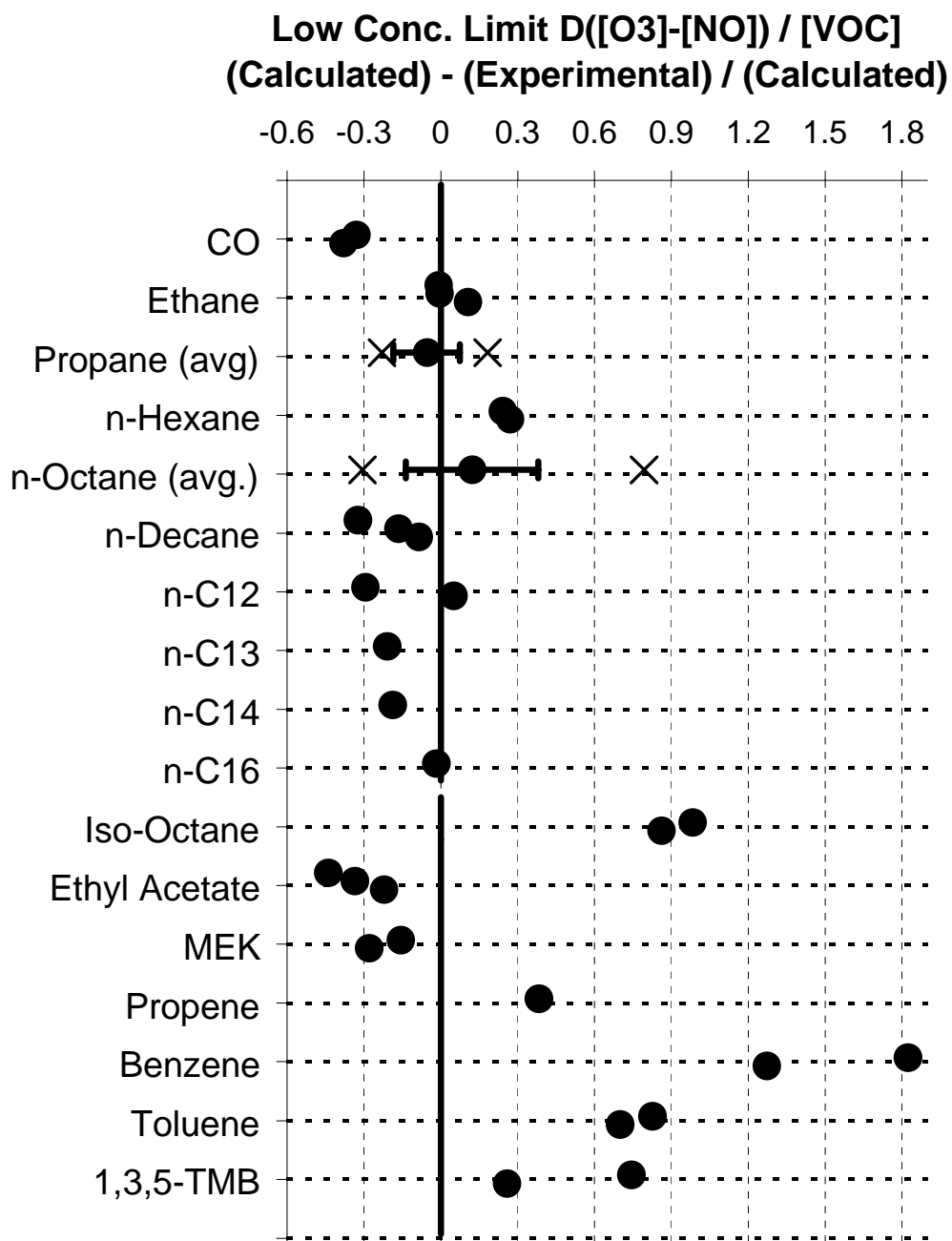
# PROBLEMS AND ONGOING WORK

## PROBLEMS

Reliability and reproducibility of the syringe pump injection system needs to be improved

GC Analysis of low volatility compounds is time-consuming and very imprecise

Apparently successful experiments with $C_{12+}$ n-alkanes could not be reproduced because of injection and analysis problems

GC Methods not suitable for quantifying complex mixtures. Need either a reliable liquid injection system or a total carbon analysis system

Difficult to improve the injection system without a continuous total carbon analysis system

## ONGOING WORK

A total carbon analysis system being developed based on catalytic conversion of VOCs to $CO_2$, and measuring $CO_2$ in $CO_2$-free air

Preliminary tests indicate that this gives good data for volatile compounds, but suggest hang-up of heavy VOCs on current converter system

# CONCLUSIONS

Measuring effects of VOCs on [$O_3$]-[NO] in HONO irradiations provides a sensitive measure of the direct effects of VOCs on $O_3$ formation

The method of Febo et al (1995) can generate the clean and stable levels of HONO required

Stirred flow experiments gave data that are not entirely consistent with model predictions

Best results were obtained in plug flow experiments using a 86 cm x 1.6 cm ID quartz tube as the reactor with a 0.6 min. reaction time

Plug flow experiments were successfully applied to n-hexadecane, suggesting it may be suitable for other low volatility compounds

But problems with reproducibly injecting and analyzing low volatility compounds must be solved before it can be routinely used for them

The plug flow system needs to be integrated with a total carbon analysis system for this to be practical for low volatility compounds or mixtures

Work on integrating a total carbon analysis to this system is underway for another CARB contract.